A Book of

ATOMIC AND MOLECULAR PHYSICS

T. Y. B.Sc. • PHYSICS (PH-334) • SEMESTER III

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V. K. DHAS
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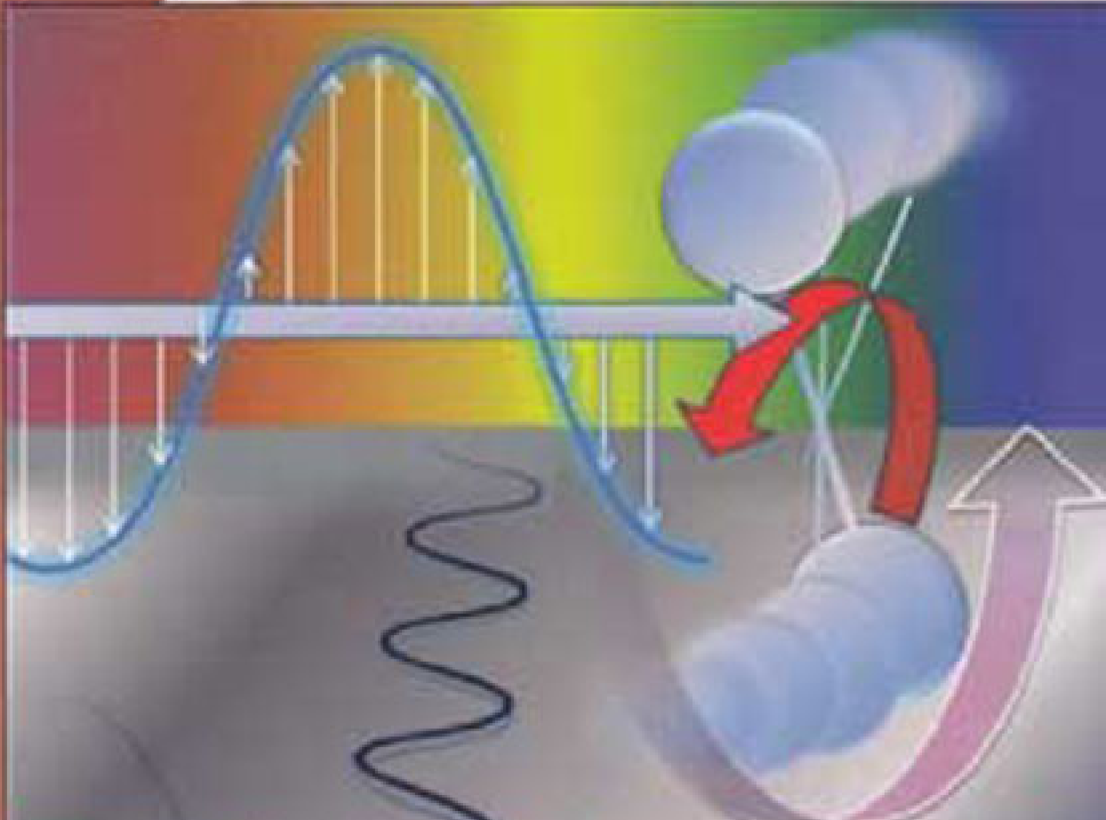

NIRALI
PRAKASHAN

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T.Y.B.Sc. Physics : PH - 334 : Semester-III

As Per New Revised Syllabus with Effect from June 2015

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Preface ...

The present book entitled **"Atomic and Molecular Physics"** is written as per new revised syllabus prescribed for the IIIrd Semester of T.Y.B.Sc. (Physics) of Savitribai Phule Pune University from June 2015. This book is targeted mainly to the undergraduate students of Pune University, but will be found useful for the graduate students and Teachers of other universities also. The book is divided into 7 chapters. Each chapter begins with basic concepts containing theory, set of formulae and explanatory notes for followed by a number of solved problems. Summary of contents in topic, short, long questions and unsolved problems are also given at the end of each topic.

The problems are judiciously selected and are given topic and section-wise. The approach is straight forward and step-by step solutions are elaborately provided. More importantly the relevant formulas used for solving the problems can be located in the beginning of each chapter. There are number of diagrams for illustration.

Chapter 1 in the book is devoted to Atomic Structure. Chapter 2 is basically concerned One Valence Electron Systems. Chapter 3 is concerned with Two Valence Electron Systems. Chapter 4 is basically related to Zeeman Effect. Chapter 5 is related to X-Ray Spectroscopy. Chapter 6 is concerned with Molecular Spectroscopy and Chapter 7 dealt with Raman Spectroscopy.

All precautions have been taken to avoid mistakes and misprint in the book. However, it is possible that some mistakes and misprints might have passed unnoticed. Such mistakes and misprint, is brought to our notice will be thankfully acknowledged.

We are thankful to Shri Jignesh Furia and staff of Nirali publication for publishing the book in attractive look. We have a pleasure to thank Mr. Santosh Bare for the bulk of typing and Mr. Kiran Velankar for proof reading. I am indebted to Mrs. Anjali Muley for line drawings, to Ravi Walodare for designing cover page and all staff in the distribution of books network.

We are also thankful to all the Marketing Staff especially Mr. Nilesh Deshmukh and others for co-ordinating the matter well in time.

Suggestions to improve the quality of the book will be gladly accepted.

JUNE 2015 **AUTHORS**

PUNE

Syllabus ...

1. Atomic Structure (6 L)

1. Rutherford's model of atom
2. Electron orbits
3. Bohr atom
4. Energy levels and spectra (1 to 4 Revision)
   Vector atom model (Concepts of space and quantization and electron spin)
5. Atomic excitation and atomic spectra, Problems.

2. One and Two Valence Electron Systems (7 L)

1. Pauli Exclusion principle and electron configuration,
   Quantum states, Spectral notations of quantum states.
2. Spin-Orbit Interaction (Single valence electron atom), Energy levels of
   Na atom, Selection rules, Spectra of sodium atom, Sodium doublet.

3. Two Valence Electron Systems (7 L)

1. Spectral terms of two electron atoms, Terms for equivalent electrons,
   LS and jj coupling schemes.
2. Singlet-Triplet separation for interaction energy of LS coupling.
   Lande's Interval rule, Spectra of Helium atom, Problems.

4. Zeeman Effect (4 L)

1. Early discoveries and developments
2. Experimental arrangement
3. Normal and anomalous Zeeman Effect problems
4. Stark effect (Qualitative discussion)

5. X-Ray Spectroscopy (6 L)

1. Nature of X-rays
2. Discrete and continuous X-ray spectra, Duane and Hunt's rule
3. X-ray emission spectra
4. Moseley's law and its applications
5. Auger effect, Problems.

6. Molecular Spectroscopy (10 L)

1. Rotational energy levels
2. Vibrational energy levels
3. Rotational and Vibrational spectra
4. Electronic spectra of molecules, Problems.

7. Raman Spectroscopy (8 L)

1. Classical theory of Raman Effect - Molecular polarizability
2. Quantum theory of Raman Effect
3. Experimental Set up for Raman Effect
4. Applications of Raman Spectroscopy.

•••

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1. ATOMIC STRUCTURE 1.1 – 1.30

2. ONE VALENCE ELECTRON SYSTEMS 2.1 – 2.26

3. TWO VALENCE ELECTRON SYSTEMS 3.1 – 3.20

4. ZEEMAN EFFECT **4.1 – 4.20**

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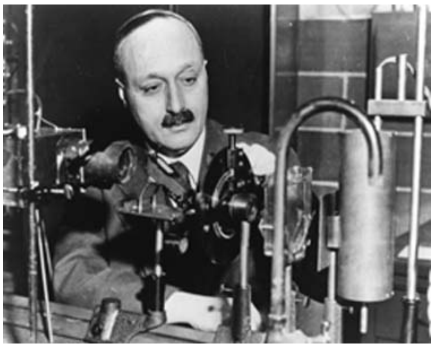
Chapter 1...

Atomic Structure

Contents ...



James Franck

James Franck (26 August 1882 – 21 May 1964) was a German physicist and Nobel laureate (with Hertz).

In 1914, James Franck and Gustav Hertz performed an experiment which demonstrated the existence of excited states in mercury atoms, helping to confirm the quantum theory which predicted that electrons occupied only discrete, quantized energy states.

Introduction

- Every atom consists of nucleus of proton and neutron with number of electrons revolving around the nucleus. It was thought that electrons revolve around the nucleus like planets do around the sun. But classical electromagnetic theory rejected possibility of stable electron orbit. To resolve this paradox Neil Bohr applied quantum theory to understand atomic structure in 1913 and developed a model which is still a convenient mental picture of an atom.
- In this chapter, the chief concern will be on Rutherford model, electron orbits, Bohr atom and energy levels. In addition vector atom model and concept of atomic excitation is discussed.

1.1 Rutherford's Model of an Atom

- Discovery of electron by J.J. Thomson provided a starting point for theories of atomic structure. J.J. Thomson assumed that an atom consisted of electron distributed in the positively charged sphere of radius 10^{-10} m. This model could not explain all features of optical spectra of hydrogen and other elements and hence the theory was discarded.

- At the suggestion of Ernest Rutherford two scientists Hans Geiger and Ernest Marsden used as probes for the fast alpha particles emitted by certain radioactive elements. Alpha particles are helium atoms that have lost two electrons each leaving them with a charge of + 2e.

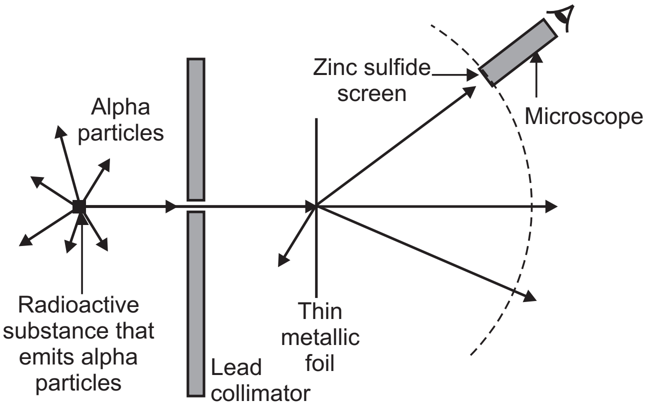


Fig. 1.1 : Rutherford's scattering experiment

- They placed a sample of a alpha-emitting substance behind a lead screen with a fine hole as shown in Fig. 1.1 so that narrow beam of alpha particles was produced. The beam was directed at a thin gold foil. Screen was made up of zinc sulphide. Screen gives off a visible flash of light when struck by alpha particle was set on the other side of the foil with a microscope to observe flashes.

- It was expected that alpha particle would go right through foil without any deviation. Geiger and Marsden observed that most of the alpha particles were not deviated by much but a few were scattered through very large angles. Some of them were even scattered in backward direction. Alpha particles are relatively heavy (≈ 8000 times mass of electron) and have a speed of 2×10^7 m/s, so it was clear that powerful forces are there which cause such remarkable deflection.

- To explain this result Rutherford put forward his model. According to the model, an atom is composed of tiny nucleus in which its positive charge and nearly all its mass are concentrated with electron some distance away. (Refer Fig. 1.2)

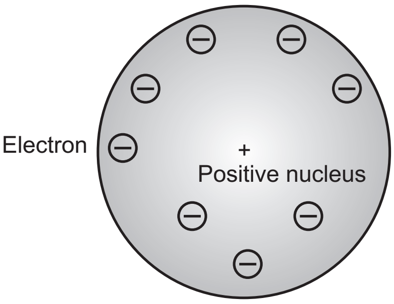


Fig. 1.2 : Rutherford's model of an atom

- When an alpha particle happens to come near a nucleus, the intense electric field there scatters it through large angle. Being electrons are light, they do not appreciably affect the alpha particles. It is also observed that the deflection of an alpha particle when it passes near nucleus depends on the magnitude of the nuclear charge. Comparing the relative scattering of alpha particles by different foils provides information about charges of an atom involved. The nuclear charges are to be multiple of +e and the number Z (called atomic number of element). We know that proton, each with charge +e, provides the charge on a nucleus, so that the atomic number of an element is the same as number of protons in the nuclei of its atom.
- The formula that Rutherford obtained for alpha particle scattering by a thin foil on the basis of nuclear model is

$$N(\theta) = \frac{N_i \, ntZ^2 e^4}{(8\pi\varepsilon_o)^2 r^2 KE^2 \sin^4(\theta/2)} \qquad \ldots (1.1)$$

where $N(\theta)$ = Number of alpha particles per unit area that reach the screen at scattering angle θ

N_i = Total number of alpha particles that reach the screen

n = Number of atoms per unit volume in the foil

Z = Atomic number of the foil atom

r = Distance of the screen from the foil

KE = Kinetic energy of the alpha particle

t = Foil thickness

- Prediction of equation (1.1) agrees with measurements of Geiger and Marsden. As $N(\theta) \propto \frac{1}{\sin^4(\theta/2)}$, the variation of $N(\theta)$ with θ is pronounced. Refer Fig. 1.3. Only 0.14% of incident alpha particles are scattered by more than 1^o.

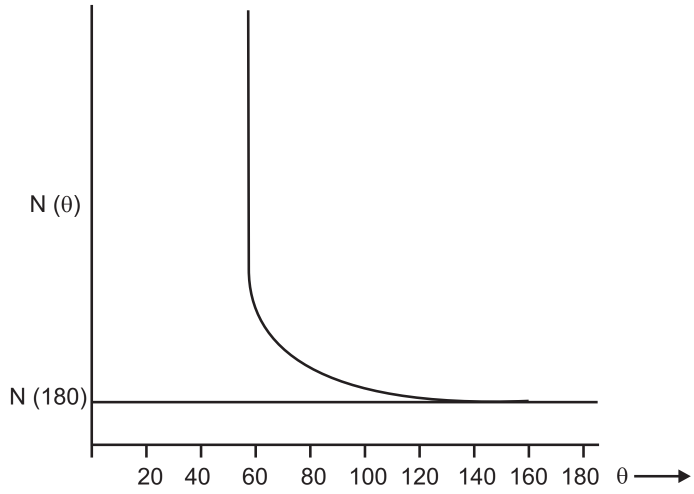


Fig. 1.3 : Rutherford's scattering N(θ) versus θ

- In the derivation of equation (1.1), Rutherford assumed that size of target nucleus is small compared with the minimum distance R to which incident alpha particles approach the nucleus before being deflected away. Thus, Rutherford's scattering gives us a way to find an upper limit of nuclear dimension.
- Let us calculate distance of closest approach R for an alpha particle. Alpha particle will have smallest R when it approaches to a nucleus head on, which will be followed by a 180^o scattering. At the instant of closest approach, the initial kinetic energy KE of particle is entirely converted to electric P.E. so that

$$\text{K.E. (initial)} = \text{P.E.} = \frac{1}{4\pi\varepsilon_o}\frac{2\,Ze^2}{R}$$

Charge on α particle = 2e and that of nucleus = Ze

∴ Distance of closest approach,

$$R = \frac{2\,Ze^2}{4\pi\varepsilon_o\,KE_{\text{initial}}} \qquad \dots (1.2)$$

In natural origin, max. K.E. = 7.7 MeV = 1.2×10^{-12} J

Taking $\frac{1}{4\pi\varepsilon_o} = 9 \times 10^9\ \text{Nm}^2/l^2$

$$R = \frac{9 \times 10^9 \times (1.6 \times 10^{-19})^2}{1.2 \times 10^{-12}} Z$$

$$= 3.8 \times 10^{-16}\ Z \text{ meter}$$

For gold, Z = 79. $R\ (AU) = 3 \times 10^{-14}$ m

- Radius of gold nucleus is less than 3×10^{-14}, well under 10^{-4} the radius of an atom as a whole.

1.2 Electron Orbits

- Rutherford's model confirms model of an atom. According to him an atom is tiny, massive, positively charged nucleus surrounded by electrons at relatively great distance to make an atom electrically neutral as whole.

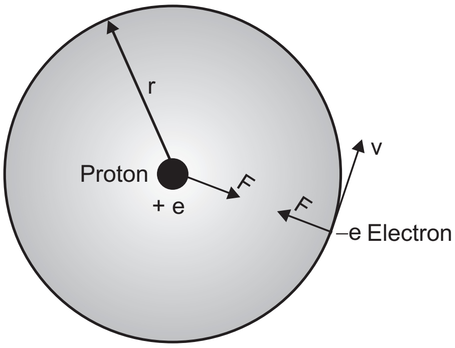


Fig. 1.4 : Force balance in a hydrogen atom

- Consider the case of a simple hydrogen atom having a single electron. We assume a circular electron orbit for convenience. The centripetal force holding electron in an orbit of radius r is given by

$$F_c = \frac{mv^2}{r}$$

Similarly, nucleus is provided by electric force.

$$F_e = \frac{1}{4\pi\varepsilon_o}\frac{e^2}{r^2}$$

Condition for a dynamic stable orbit is

$$F_c = F_e$$

$$\frac{mv^2}{r} = \frac{1}{4\pi\varepsilon_o}\frac{e^2}{r^2}$$

Hence velocity v related to orbital radius is

$$v = \frac{e}{\sqrt{4\pi\varepsilon_o\, mr}} \qquad \text{... (1.3)}$$

- Total energy of hydrogen atom is the sum of kinetic and potential energies.

$$\text{K.E.} = \frac{1}{2}mv^2 \quad \text{and} \quad \text{P.E.} = -\frac{e^2}{4\pi\varepsilon_o\, r}$$

$$E = \text{K.E.} + \text{P.E.} = \frac{mv^2}{r} - \frac{e^2}{4\pi\varepsilon_o\, r}$$

Substituting the value of v from equation (1.3),

$$E = \frac{e^2}{8\pi\varepsilon_o r} - \frac{e^2}{4\pi\varepsilon_o r}$$

Total energy of an hydrogen atom

$$E = -\frac{e^2}{8\pi\varepsilon_o r} \qquad \text{... (1.4)}$$

- Total energy of an hydrogen atom is negative. This holds for every atomic electron and reflects the fact that it is bound to the nucleus. If $E > 0$, and electron would not follow a closed orbit around nucleus.
- The above analysis is an application of Newton's law of motion and Coulomb's law of electric force. Both laws are pillars of classical physics and is in accord with the experimental observation that atoms are stable.
- But it is not in accord with electromagnetic theory, another pillar of classical theory. According to electromagnetic theory the accelerating electric charges radiate energy in the form of wave. An electron pursuing a curved path is accelerated and therefore should continuously lose energy into nucleus in a fraction of second. (Refer Fig. 1.5) But atoms do not collapse. The laws of physics that are valid in macroworld do not hold true in the microworld of atom.

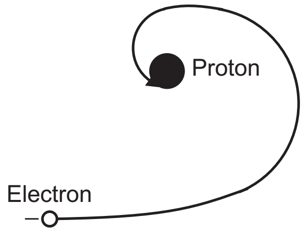


Fig. 1.5

- Classically atomic electron spiral rapidly into the nucleus as it radiates energy due to its acceleration.
- Thus, classical physics fails to provide a meaningful analysis of atomic structure because it approaches the nature in terms of pure particles and pure waves. In reality, particles and waves have many properties in common though the smallness of Planck's constant make the wave particle duality imperceptible in the macroworld. The usefulness of classical physics is less for microworld, we must allow particle behaviour of waves and wave behaviour of particle to understand atom. In remaining sections of the topic, we will see how the Bohr's atomic model which combines classical and modern approach.

1.3 Bohr Atom

- The hydrogen atom theory proposed by Neil Bohr in 1913, marked the beginning of a new era in atomic structure and spectroscopy. Bohr's theory provided the satisfactory explanation of the Balmer, Lyman, and Paschen series of hydrogen atom and the

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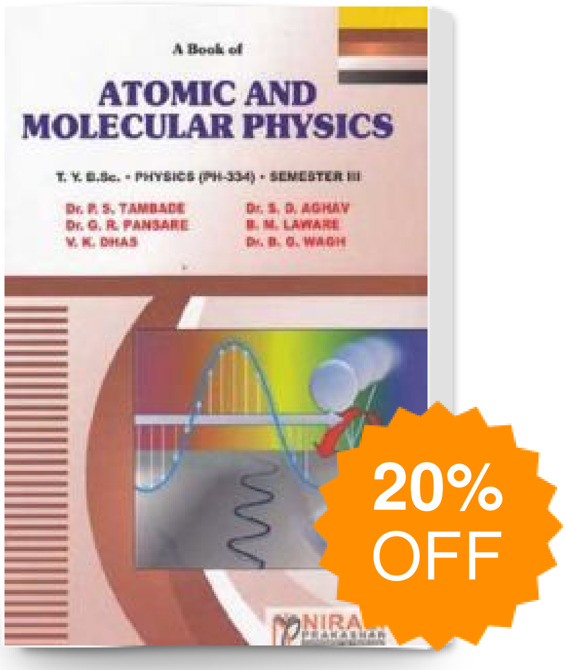

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